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Some Physicochemical and Environmental Factors Affecting Transformation Rates and Sorption of the Herbicide Metamitron in Soil

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Abstract: In addition to the molecular structure of a pesticide, environmental conditions may influence its persistence through their effect on the growth and activity of pesticide-degrading micro-organisms. As a result, transformation rates may decrease rapidly when a compound is leached into subsoil. Metamitron sorption isotherms were determined and incubation series were set up for a sandy loam soil, simulating single and combination effects that occur during transport of metamitron into subsoils. K_{OC} values increased with increasing depth from 185 to 700 litre kg^{-1}. A combination of conditions that are unfavourable for microbial activity, such as low temperature (5°C), low concentrations (0·5 mg kg^{-1}) and a large sorbed fraction (K_{OC} = 700) resulted in half-lives of over one year. Oxygen inhibition decreased the transformation rate of metamitron from 0·058 to 0·019 day^{-1}. In order of significance, the transformation of metamitron appears to be a function of temperature, oxygen availability and sorption to organic carbon. Increasing doses did not change transformation rates significantly, although different transformation pathways were observed.

Key words: pesticides, environmental risks, transformation, sorption, persistency.

1 INTRODUCTION

The transformation rate of a pesticide in the environment is related to its molecular structure and chemical properties. The complexity or length of its structure may be expressed numerically by the molecular connectivity index (MCI), described by Sabljic,[1] and requires the summation of the number of bonding sites within the non-hydrogen part of the molecular skeleton, according to $\Sigma(nP_i)^{-0.5}$ in which P is a pair of adjacent bonding sites and n the occurrence of this pair. Based on the assumption that a large, complex molecule generally has a larger number and more diverse arsenal of bonding types, it is expected that the overall sorption strength is larger than for simple molecules like alkanes. Hence, the bio-availability in pore water may be lower. Based on this assumption, Shaaban and Elprince[2] used the MCI as a substitute for K_{OC}. If a reliable value of K_{OC} is not available, the MCI may be a useful tool to estimate the persistence of a pesticide.

For the chemical breakdown of pesticides, an activation energy is required to separate the bondings. A classic method to describe the speed of chemical reactions is expressed by the Arrhenius function:

$$\mu = Ae^{-E_a/RT} \quad (1)$$

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in which μ is the reaction rate, A is the frequency factor of chemical interactions, E_a is the activation energy in kJ K^{-1} $mole^{-1}$, R is the gas constant and T is the absolute temperature. The variable A can be eliminated mathematically if μ is determined for at least two temperatures:

$$\text{for } T_2 > T_1: \quad \begin{cases} \ln \mu_1 = \ln A - \dfrac{E_a}{RT_1} \\ \ln \mu_2 = \ln A - \dfrac{E_a}{RT_2} \end{cases} \qquad (2)$$

In which μ_1 and μ_2 are transformation rates at temperature T_1 and T_2 (K). This results in:

$$\ln \frac{\mu_2}{\mu_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (3)$$

which enables the calculation of E_a. The activation energy is proportionally related to a compound's persistence (DT_{50}). Aromatic structures, as found in triazine pesticides, among others, are generally characterized by large MCI values as well as a high activation energy. Table 1 gives, for metamitron and some other widely applied pesticides, a comparison between the characteristic molecular connectivity index and the activation energy. Although there is some uncertainty in the intermediate area, induced by length rather than complexity of the molecule, there appears to be an increasing concave relationship.

Besides these structure-related conditions, the overall transformation of pesticides is highly regulated by environmental factors. In this study, we consider the herbicide metamitron (4-amino-4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazin-5-one, 'Goltix', Fig. 1). Metamitron is a selective systemic herbicide (photosynthesis inhibitor) which is widely used for the control of broad-leaved weeds and grasses in beet and flower bulbs. Application rates vary between 2 and 6 kg ha^{-1} (700 g kg^{-1} formulation; 1·8 g $litre^{-1}$ solubility in water). The compound is characterized by its relatively complex molecular structure and large activation energy, and may thus potentially be resistant to transformation under certain conditions. To micro-organisms, metamitron may act as a nitrogen source. The main metabolite of metamitron is formed after the cleavage of the amino group, giving 3-methyl-6-phenyl-1,2,4-triazin-5(4*H*)-one. Transformation rates may decrease when an alternative nitrogen source is readily available, or when physicochemical impediments occur. This is likely to happen when the compound is leached into other, low-oxygeneous systems like subsoils or ground waters and surface waters. It may be stated that environmental conditions that inhibit the growth and activity of micro-organisms may decrease transformation rates of metamitron. However, there is little agreement on the quantitative effects of environmental factors of metamitron transformation. Bond and Roberts[9] concluded that temperature may be more important than soil moisture in limiting degradation of metamitron. Walker and Brown[10] concluded that transformation rates were correlated with microbial biomass and not with soil respiration. Allen and Walker[11] found that the availability of metamitron in the soil solution was of particular importance. Also, the rate of loss may be related to the rate and strength of sorption of the herbicide by soil solids, thus protecting it from being transformed by micro-organisms. This study focuses on the microbial transformation and sorption sensitivity of metamitron, as regulated by temperature, oxygen availability, sorption to soil colloids and concentration of the compound. Incubations of samples of a sandy loam

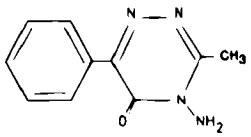

Fig. 1. Metamitron.

TABLE 1
Molecular Connectivity Index (MCI) and Activation Energy (E) for Several Pesticides

Compound	*MCI*	*E(act)* (*kJ K^{-1} $mole^{-1}$*)	*Reference*
1,3-Dichloropropene	2·41	12·2	3
Mecoprop-P	5·10	25	Estimated
Aldicarb	5·51	22·4	4
2,4-D	5·68	34·4	3
Simazine	6·25	45; 57·4	5; 6
Metribuzin	6·37	59·0	7
2,4,5-T	6·50	85·0	7
Atrazine	6·61	44·0	8
Oxamyl	6·70	67·3	4
Metamitron	7·19	86·7; 127·3	9; this work
DDT	8·87	>300	Estimated

soil were used to simulate single effects and combination effects on transformation rates.

2 MATERIAL AND METHODS

2.1 Soil samples

From a calcareous Fluvisol (sandy loam) in a field in the North-east polder, The Netherlands, soil samples were taken of four layers (5–15, 25–35, 45–55 and 65–75 cm). These layers reflect the geomorphological horizons of the soil profile (marine, brackish and fresh water deposits). Soil properties are summarized in Table 2. In previous years, the soil had been treated periodically with metamitron, and it is likely that a population of micro-organisms able to transform metamitron has developed. Residual metamitron concentrations in the samples were below the detection limit of 0·01 mg kg^{-1} dry weight.

2.2 Adsorption series

Partitioning of metamitron over the solid and liquid phases for the four layers was determined for a wide concentration range, emphasizing the lower concentration range that is field-realistic. Standard solutions contained 1, 5, 10, 100, 500 and 1000 μg $litre^{-1}$ metamitron (active ingredient) in 0·01 M calcium chloride. Standard solutions, soil samples and batch mixtures were kept at 5°C to minimize transformation during the experiment. The soil/liquid ratio was 0·5, which is in agreement with the recommendations made by Boesten.[12] A high solid/liquid ratio has the additional advantage that sorption kinetics proceed more rapidly.[13] The samples were shaken linearly (192 movements per minute, 6·5 cm amplitude) for 6 h, left overnight for 16 h and shaken again for 1 h, all at 5°C. After centrifugation at 1500 g for 10 min, an aliquot of 60 ml extract was pipetted, extracted with dichloromethane and purified over florisil. A two-column HP 5880-GC was used for duplicate analyses.

2.3 Incubation series

To simulate oxygen inhibition during microbial transformation of the compound, as would occur after leaching into subsoils, open and closed incubation series were set up. To 50-g samples of each layer ($\theta \approx 0{\cdot}25\%$), a quantity of metamitron was added that would reflect a realistic concentration decrease in depth, based on field observations in previous years. This resulted in a dose of 2 mg kg^{-1} for the first layer, 1 mg kg^{-1} for the second layer and 0·5 mg kg^{-1} for the third and fourth layers. Separate vials were used for each observation (1 h, 1, 3, 7, 15, 35 and 70 days) and were tightly sealed with a ground glass stopper and stored at 5°C. An identical series of samples was stored at 15°C. This resulted in a total of 56 incubation vials. The available oxygen in the incubation vials was $7{\cdot}4 \times 10^{-4}$ mole O_2, which corresponds to an oxidation energy of approximately 0·2 kJ.

A similar experiment was done with seven samples of the top soil layer (5–15 cm) and four concentrations (10, 4, 2, 0·5 mg kg^{-1}). In this test, the 28 flasks were loosely stoppered with glass wool to allow diffusive exchange of oxygen, and stored at 15°C. If necessary, water was added corresponding to the loss of weight in random checks.

3 RESULTS AND DISCUSSION

Adsorption isotherms were described with the Freundlich equation:

$$q = K_f C_e^n \tag{4}$$

in which q is the sorbed amount in mg kg^{-1}, C_e is the equilibrium concentration of the water phase in mg $litre^{-1}$, K_f and n are experimental constants, which represent the intercept and the slope of the linearized logarithmic isotherm when presented as $\log q = \log K_f + n \log C_e$. Freundlich parameters and corresponding measurements/curve-fit correlation coefficients are presented in Table 2. Note the gradual but significant increase of K_{OC} as depth increases, which is possibly a result of a higher degree of humification and reactivity of the soil organic phase.

In Fig. 2, measurements on similar soils carried out by Allen and Walker[11] and Goicolea *et al.*[14] were used

TABLE 2
Soil Properties and Freundlich Parameters

Soil layer (*cm*)	*<2 μm* (%)	*Organic carbon* (%)	*Calcium carbonate* (%)	pH_{H_2O}	*Freundlich parameters*			
					n	K_f	K_{OC}	r
1: 5–15	6·4	1·1	5·90	7·8	0·90	2·04	185	0·959
2: 25–35	6·6	1·0	5·20	7·8	0·87	2·29	229	0·959
3: 45–55	6·3	0·9	5·45	7·8	0·84	3·72	413	0·979
4: 65–75	4·8	0·9	6·85	7·8	0·81	6·30	700	0·985

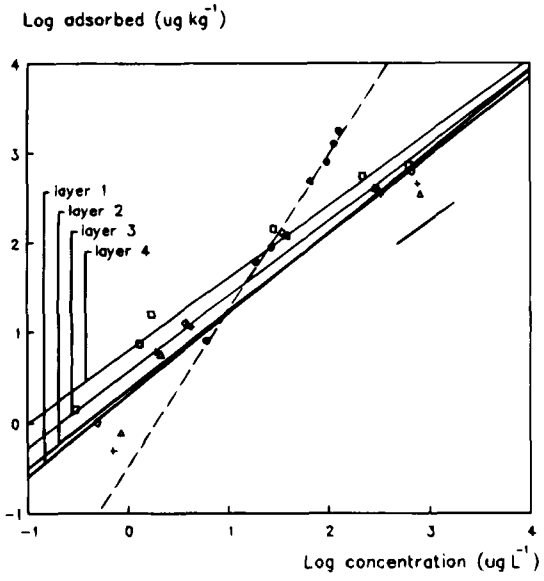

Fig. 2. Adsorption isotherms of metamitron in soil layers 1–4 and as reported by (——) Allen and Walker[11] and (– – –) Goicolea *et al.*[14] Sample properties and corresponding Freundlich parameters are:

	<2 μm	*Organic carbon* (%)	*pH*	*n*	K_f	K_{oc}
Allen and Walker[11]	15	0·6	6·3	0·76	1·5	250
Goicolea *et al.*[14]	25	1·9	7·6	1·71	0·3	16
Layers 1–4: Table 2						

for comparison. Organic carbon contents range from 0·6 to 1·9. The fact that Goicolea *et al.* found $K_f = 0{\cdot}3$ and $n = 1{\cdot}71$ may be the effect of a relatively high organic carbon content with a low sorption capacity. Consequences of the observed concentration ranges (1000–5000 μg litre^{-1} by Allen and Walker, 100–1000 μg litre^{-1} by Goicolea *et al.* and 1–1000 μg litre^{-1} in this study) are clearly expressed by the (un)certainty of the exact intercept value, resulting in K_f, and the representativeness of the slope (n) for a wide concentration range.

The consumption of oxygen is expressed in the two pathways in Fig. 3. It shows that transformation rates during the first ten days do not differ much between the two incubation series, and transformation at oxygen saturation is well described ($r = 0{\cdot}997$) by a simple first-order equation:

$$\frac{d}{dt}(P) = -\mu \cdot P \tag{5}$$

In which P is the total amount of metamitron in soil and soil solution and μ is the specific transformation rate.

However, differences in DT_{90} values at saturated and low oxygen concentrations prove to be significant, which implies high persistency of residual concentrations at low oxygen concentrations. This type of transformation could not be described with eqn (5). Under limiting oxygen concentrations, we assume that the specific growth rate of strictly aerobic micro-organisms depends on the dissolved oxygen concentration $[O_2]$ according to the Monod equation:[15]

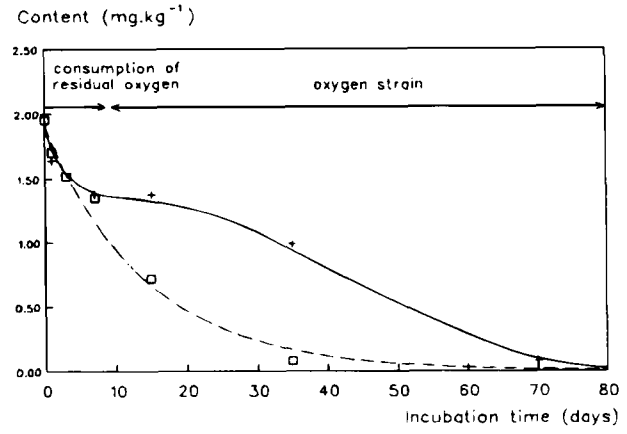

Fig. 3. Metamitron transformation in the 5–15 cm soil layer at (□) open and (+) closed incubations. Experimental conditions, temperature (15°C) soil properties (<2 μm = 6·4%, organic carbon = 1·1%, pH = 7·8), dose (2 mg kg^{-1} dw) and moisture content (0·25% w/w) are identical.

$$\mu = \frac{\mu_{max}[O_2]}{(K_s + [O_2])} \tag{6}$$

In which μ_{max} is the maximum specific growth rate and K_s is the Monod half-saturation constant. By further assuming that transformation of the compound mainly occurs for the dissolved fraction, eqn (5) may be modified if combined with eqn (4), and defining P as:

$$\begin{cases} \dfrac{d}{dt}(P) = -\mu C(t) \\ P = \theta C(t) + \rho K_f [C(t)]^n \end{cases} \tag{7a, b}$$

in which θ is the water fraction, $C(t)$ is the time-dependent concentration and ρ is the soil bulk density (g cm^{-3}). A major obstacle for the quantification of the inhibitory effect of oxygen on the growth of micro-organisms is that the concentration of oxygen in the solution has to be monitored, if detectable, under these low oxygen conditions. Furthermore, slowly decreasing oxygen concentrations, as were simulated in this experiment, require dynamic coupling of eqns (6) and (7a, b).

Boesten *et al.*[16] concluded from experiments with water-saturated sediments that certain compounds may be very stable in aqueous, low-oxygenous systems. Ashley and Leigh[17] and Gerstl *et al.*[18] reported similar findings. These results indicate that in low-oxygenous conditions the microbial contribution in the total transformation is slowed down or eliminated, and that transformation in low-oxygenous environments is likely to be of a chemical rather than of a microbiological nature.

The results of the first incubation series are presented in Table 3, in which a relation is made between the soil layer, its specific sorption coefficient related to organic carbon, dose and temperature. Note the significant decrease of transformation rates at 5°C at a combination of low concentrations and high sorption. The difficulty in determining causal relationships for field conditions is obvious. One-parameter interpretations of results of incubation tests may not be justified, since physicochemical properties of both soil and compound, and the specific population dynamics of micro-organisms may be (inversely) correlated.[3,19]

A formula describing the influence of temperature on the specific transformation rate is given by O'Neill,[20] and assumes a maximum transformation rate at the temperature with the highest microbial activity. This formula was used by many authors[3,19,21] and resulted in the determination of optimum temperatures for rapid transformation of several pesticides. Other formulae,[22] including the Arrhenius function (eqn (1)) appeared to be less accurate.

Figure 4 shows the dynamic patterns of transformation pathways as a function of concentration (incubation series II). At low concentrations, transformation can be expressed by a first-order model (eqn (5), Fig. 4b). At concentrations higher than 4 mg kg^{-1}, three phases may be recognised: an initial lag-phase, with sub-optimum transformation rates, a phase of accelerated transformation, and a third phase which is characterized by decreasing transformation rates as a result of substrate inhibition and microbial competition. This type of transformation (Fig. 4a) could be described by a modified non-linear model.[19] Dependent on the pesticide, this effect may be more or less pronounced. In general, this type of transformation is more effective in degrading residual concentrations, since microbial activity has been boosted to its optimum during previous higher concentrations.[3,19,21] In this test, residual concentrations after 35 days of 4 and 6% were measured for the high doses, and 20 and 18% for the low doses.

Results indicate that the transformation of metamitron is mainly regulated by microbial activity, controlled by temperature and the availability of both oxygen and substrate. A combination of unfavourable microbial conditions, such as low temperature (5°C), low concentrations (0·5 mg kg^{-1}) and high sorption capacity (K_{OC} = 700) resulted in half-lives of over one year. Oxygen inhibition decreased the transformation rate from 0·058 to 0·019 day^{-1}.

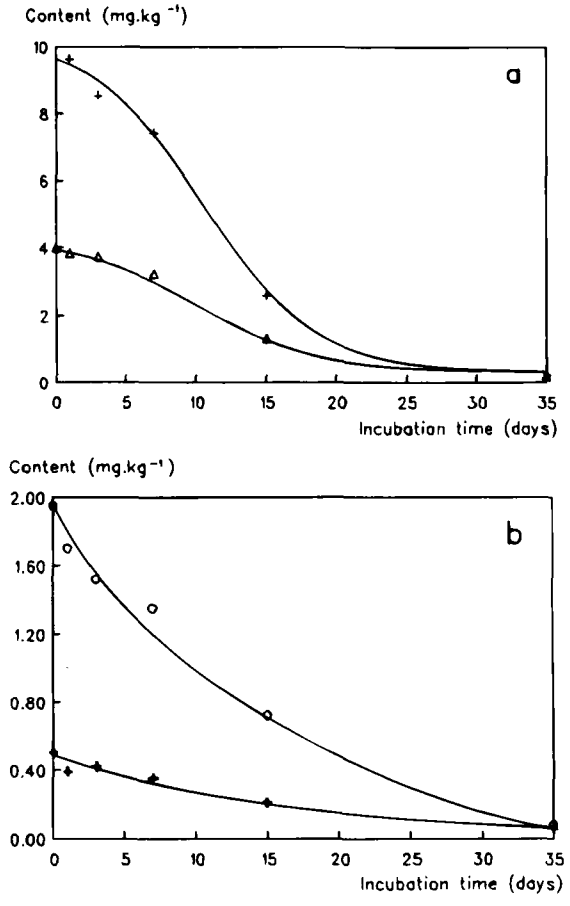

Fig. 4. Transformation pathways at (a) high and (b) low metamitron contents without oxygen limitation. Application rates were (+) 10, (△) 4, (○) 2 and (+) 0·5 mg kg^{-1}. Although half-lives do not vary significantly (11, 13, 8 and 12 days, respectively), the descriptive equations originate from different dynamics.

To quantify the effects of the various environmental factors, the data were combined and subjected to factor analysis and paired *t*-tests. In order of statistical significance (0·95 confidence interval), the transformation of metamitron appears to be a function of temperature, oxygen availability and sorption to organic carbon. Increasing doses (0·5, 1·0, 4·0 and 10·0 mg kg^{-1}) did not change transformation rates significantly, although different transformation pathways were observed. Hence, $\mu = f(T, Ox, K_{OC})$ and $\mu \neq f(Dose)$, in which μ is the specific transformation rate of metamitron. For these parameters, some formulations are summarized in Table 4. For metamitron, the significance of temperature was also emphasized by Bond and Roberts.[9]

TABLE 3
Dose, Organic Carbon Sorption Coefficient and Half-Lives for Metamitron at Two Temperatures

Soil layer	*Dose (mg kg^{-1})*	K_{OC}	*Half-lives (days)* 5°C	15°C
1	2·0	185	61	9
2	1·0	229	140	5
3	0·5	413	>1 yr	41
4	0·5	700	>1 yr	68

TABLE 4
Specific Transformation and Growth Rate (μ) Formulations Tailored to Environmental Factors

Environmental factor	*Formulation*	*Function (ref.)*
Temperature	$\mu(T) = \begin{cases} \mu_{max}\left(\frac{T_{max} - T}{T_{max} - T_{opt}}\right)^{a} \cdot \exp\left(\frac{a(T - T_{opt})}{T_{max} - T_{opt}}\right) & \text{for } T > T_{min} \wedge T < T_{max} \\ 0 & \text{for } T \leqq T_{min} \wedge T \geqq T_{max} \end{cases}$	O'Neill (3, 20, 21)
Oxygen	$\mu = \frac{\mu_{max}[O_2]}{(K_s + [O_2])}$	Monod (15)
Availability in soil solution	$\mu(t) = \ln \frac{P_{(t)}}{C_{(t)}} \Big/ t$ with $P = \theta C(t) + \rho K_f[C(t)]^n$	First-order + Freundlich (2, 6)
High dose	$\mu(t) = \ln \frac{P_{(t)}W}{P_{(0)} - P_{(t)}} \Big/ t$	Modified non-linear (19)
Low dose	$\mu(t) = \ln \frac{P_{(t)}}{P_{(0)}} \Big/ t$	First-order (19)

μ_{max} = Maximum rate
T_{max} = Lethal temperature
T_{min} = T below which microbial activity is negligible
T_{opt} = T with maximum microbial activity
$[O_2]$ = Dissolved oxygen concentration
a, W = Experimental parameters
K_s = Monod half-saturation constant
K_f, n = Freundlich parameters
P = Pesticide quantity, initial (0), at time t (t)
θ = Water content
ρ = bulk density
$C(t)$ = Pesticide concentration at time t

The availability of the compound appears to be of less consequence, whereas the application rate of metamitron appears to be non-discriminating.

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REFERENCES

1. Sabljic, A., Prediction of the nature and strength of soil sorption of organic pollutants by molecular topology. *J. Agric. Food Chem.*, **32** (1984) 243–6.
2. Shaaban, Z. & Elprince, A. M., A simulation model for the fate of pesticide residues in a field soil. *Plant Soil*, **114** (1989) 187–95.
3. Vink, J. P. M., Nörtersheuser, P., Richter, O., Diekkrüger, B. & Groen, K. P., Modelling the microbial breakdown of pesticides in soil using a parameter estimation technique. *Pestic. Sci.*, **40** (1994) 285–92.
4. Bromilow, R. H., Baker, R. J., Freeman, M. A. H. & Görög, K., The degradation of aldicarb and oxamyl in soil. *Pestic. Sci.*, **11** (1980) 371–8.
5. Smith, A. E. & Walker, A., A quantitative study of asulam persistence in soil. *Pestic. Sci.*, **8** (1977) 449–56.
6. Walker, A., Simulation of herbicide persistence in soil. II. Simazine and linuron in long-term experiments. *Pestic. Sci.*, **7** (1976) 50–8.
7. Walker, A. & Smith, A. E., Persistence of 2,4,5-T in a heavy clay soil. *Pestic. Sci.*, **12** (1979) 151–7.
8. Smith, A. E. & Walker, A., Prediction of the persistence of the triazine herbicides atrazine, cyazine and metribuzin in Regina heavy clay soil. *Canad. J. Soil. Sci.*, **70** (1989) 485–91.
9. Bond, W. & Roberts, H. A., Persistence of metamitron in a sandy loam soil. *Bull. Environ. Contam. Toxicol.*, **16** (1976) 431–6.
10. Walker, A. & Brown, P. A., *Proceedings EWRS Symposium Theory and Practice of the Use of Soil Applied Herbicides*, 1981, pp. 63–71.
11. Allen, R. & Walker, A., The influence of soil properties on the rates of degradation of metamitron, metazachlor and metribuzin. *Pestic. Sci.*, **18** (1987) 95–111.
12. Boesten, J. J. T. I., Influence of solid/liquid ratio on the experimental error of sorption coefficient in pesticide/soil systems. *Pestic. Sci.*, **30** (1990) 31–41.
13. Boesten, J. J. T. I. & Van der Pas, L. J. T., Modeling adsorption/desorption kinetics of pesticides in a soil suspension. *Soil Sci.*, **146** (1988) 221–31.
14. Goicolea, M. A., Arranz, J. F., Barrio, R. J. & De Balugera, G., Adsorption-leaching study of the herbicides metamitron and chloridazin. *Pestic. Sci.*, **32** (1991) 259–64.
15. Owens, J. D. & Legan, J. D., Determination of the Monod substrate saturation constant for microbial growth. *FEMS Microbiol. Rev.*, **46** (1987) 419–32.

16. Boesten, J. J. T. I., Van der Pas, L. J. T., Smelt, J. H. & Leistra, M., Transformation rate of methyl isothiocyanate and 1,3-dichloropropene in water-saturated sandy subsoils. *Neth. J. Agric. Sci.*, **39** (1991) 179–90.
17. Ashley, M. G. & Leigh, B. L., The action of metham-sodium in soil. I. Development of an analytical method for the determination of methyl isothiocyanate residues in soil. *J. Sci. Food. Agric.*, **14** (1963) 148–53.
18. Gerstl, Z., Mingelgrin, U. & Yaron, B., Behaviour of vapam and methyl isothiocyanate in soils. *Soil. Sci. Soc. Am. J.*, **41** (1977) 545–8.
19. Vink, J. P. M. & Groen, K. P., Mathematical descriptions of accelerated transformation of 1,3-dichloropropene in soil: a microbiological assessment. *Sci. Tot. Environ.*, **123/124** (1992) 591–603.
20. O'Neill, R. V., Population energetics of a millipede, *Narceus americanus. Ecology*, **49** (1969) 803–9.
21. Richter, O., Nörtersheuser, P. & Diekkrüger, B., Modeling reactions and movement of organic chemicals in soils by coupling of biological and physical processes. *Modeling Geo-Biosph. Processes*, **1** (1992) 95–114.
22. Logan, J. A., Wollkind, D. J., Hoyt, S. C. & Tanigoshi, L. K., An analytical model for description of temperature-dependent rate phenomena in arthropods. *Environ. Entomol.* **5** (1976) 1133–40.